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Model for icosahedral aperiodic graphite structures

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We apply a general procedure for generating crystalline and quasicrystalline atomic structures to fullerenes. We have found different periodic, and aperiodic graphitic structures with high stability. These structures present negative, positive, and zero Gaussian curvatures. Energetic and geometrical properties of these hypothetical structures are explained.

The discovery of crystals of C_{60} and C_{70} (Ref. 1) opens a field of possibilities for materials. Different morphologies in C_{60} and C_{70} structures such as tenfold-symmetry rods and multiple twins with icosahedral shapes[2,3] indicate that these fullerenes can have the same behavior as atoms in a conventional structure forming crystals, twins, compounds, etc. Another important fact concerns coalescence reactions in fullerenes. It has been observed by Yeretzian and co-workers that C_{60} and other fullerenes interact to form bigger stable fullerenes.[4–6] The coalescence of these structures can have important implications in growth mechanisms for materials. In this work, we explain how to get possible graphitic structures by using the two basic ideas mentioned above: first, that fullerenes can be seen as having the same role as atoms in a structure, and second, that fullerenes can interact and coalesce to get a more stable arrangement. We have used the ideas of the decahedral-recursive (DR) growth model originally applied in metals to produce both crystalline and quasicrystalline structures[7–9] to generate aperiodic arrangements of truncated fullerenes forming internal labyrinths with positive, negative, and zero Gaussian curvatures. Some of the negatively curved periodic graphite structures reported by Mackay, Terrones, and O'Keefe[10–12] can be easily obtained with this method. It can also be applied to get continuous aperiodic surfaces which can play an important role in water-lipid-surfactant systems.[13] These hypothetical aperiodic graphitic structures are highly stable and represent highly feasible new types of materials.

According to the DR model, starting from a fullerene as a "seed," the method consists of two steps: (1) translating this fullerene onto a position such that the original and the translated fullerene have coincident atoms (note that in contrast with its previous application in metals, no interpenetration is allowed here);[7,14] and (2) removing atoms with bonds at forbidden angles and repeating step (1). Since C_{60} is the most favorable fullerene, we have used it first. There are different ways of joining C_{60}. We have chosen the twofold and threefold axes as joining sites because the pentagonal rings, necessary to close the structure, are removed to make room for octagonal and heptagonal rings which are more stable (closer in energy to graphite). Ajayan and Iijima have found that in the presence of oxygen and temperatures of the order of 400 °C the pentagonal rings in graphite tubules are destroyed when producing tubes with open tips,[15] so under certain conditions pentagonal rings are not as stable as graphitic bonds.

There are 30 possibilities for choosing the twofold sites which form an icosidodecahedron. If only six mutually orthogonal sites are selected, the *P* surface (*P*688) proposed by O'Keeffe, Adams, and Sankey[12] is obtained. An alternative strategy consists of choosing randomly between the 30 vertices of the icosidodecahedron with the only restriction of no overlapping between neighboring C_{60}'s. This yields a closed nonperiodic structure with icosahedral symmetry and with internal labyrinths which resemble the labyrinths in ordered graphite foams with negative curvature[10,11,16,12,17] (see Fig. 1). For the threefold option there are 20 equivalent sites producing a dodecahedron and an analogous procedure can be applied for this case.

When using the twofold axes, two pentagonal rings disappear to generate octagonal rings with negative curvature. If the threefold axes are used then three pentagons are removed and heptagonal rings are generated [see Figs. 2(a) and 2(b)]. The angles in the octagonal and hep-

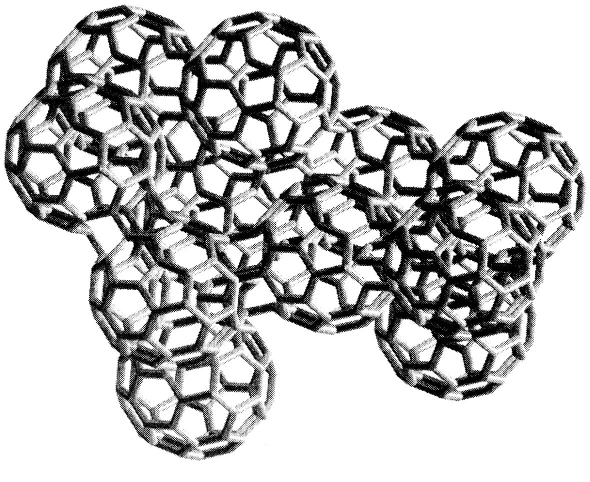

FIG. 1. Aperiodic structure with 592 atoms generated by joining the twofold sites of C_{60}.

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tagonal rings are close to 120° and the bond length of C-C in graphite (1.42 Å) is preserved. If C_{240} is used instead of C_{60} as a seed, the possibilities for joining these fullerenes are again along twofold and threefold axes. When six mutually orthogonal twofold directions are selected, the *P* surface of Mackay and Terrones can be constructed.[10,11] Aperiodic foams can be also obtained by selecting randomly between the 30 twofold or the 20 threefold possibilities not allowing interpenetration of neighboring C_{240}'s. It is also possible to use higher fullerenes such as C_{540} to generate an inflation (process of adding hexagons preserving the topology of the structure) of the P surface with 432 atoms per cubic unit cell. Therefore, in this way, different sizes of graphite layers can be built.

The graphite foams constructed with the above recipes can be adequately described as a network (centers of fullerenes) plus decoration (truncated fullerenes), so that the random tiling ideas developed in the field of quasicrystals (for a review, see Ref. 18) can be imported and directly applied to describe in a nice way some symmetry and diffraction properties of the structures, regardless of considerations of the stabilization by entropy which is the core of the random tiling model.

The coordinates of each center of fullerene can be expressed as an integer combination of vectors pointing to the vertices of an icosidodecahedron (twofold case) or a dodecahedron (threefold case). Hence, in general, the position of each node of the network can be written as $\mathbf{x}^{\parallel}=\sum_{i=1}^{6} z_i \mathbf{e}_i^{\parallel}$, where $\mathbf{e}_i^{\parallel}$ are the vertices of an icosahedron and $z_i \in Z$. Consequently, each node may be assigned integer coordinates $\{z_i\}$ which can be viewed as points in a six-dimensional cubic lattice. We can also define a complementary basis $\{\mathbf{e}_i^{\perp}\}$ such that each basis vector of R^6 can be decomposed as $\mathbf{e}_i^{\parallel}\oplus\mathbf{e}_i^{\perp}$, so that for each node $\mathbf{x}^{\parallel}$, we define a coordinate $\mathbf{x}^{\perp}$, in a "perpendicular" three-dimensional space, as $\mathbf{x}^{\perp}=\sum_{i=1}^{6} z_i \mathbf{e}_i^{\perp}$. The network of centers of fullerenes can be viewed as nodes of a six-dimensional cubic lattice by lifting up the three-dimensional coordinates $\mathbf{x}^{\parallel}$. The lifted network forms a faceted surface in six dimensions which contains all the information on symmetry and diffraction properties of the three-dimensional structure. As an approximation, this surface can be parametrized as $\mathbf{x}^{\perp}\approx\mathbf{E}\mathbf{x}^{\parallel}+\bar{\mathbf{h}}$,[18] where $\mathbf{E}$ is a 3×3 tensor which defines the orientation of the surface and is called the "phason strain." $\mathbf{E}=\mathbf{0}$ corresponds to a perfect icosahedral symmetry of the projected structure.[18]

The reciprocal-lattice vectors of the structure are projections of the six-dimensional reciprocal-lattice vectors defined by $\mathbf{k}\cdot\mathbf{x}=\mathbf{k}^{\parallel}\cdot\mathbf{x}^{\parallel}+\mathbf{k}^{\perp}\cdot\mathbf{x}^{\perp}=0 \pmod{2\pi}$. In terms of the phason strain, the peaks of the diffraction pattern of the structure have positions $\mathbf{Q}=\mathbf{k}^{\parallel}+\mathbf{E}^{T}\mathbf{k}^{\perp}$. We observe that if $\mathbf{E}\neq\mathbf{0}$, the peaks in the reciprocal space are shifted from the icosahedral ideal positions, indicating that the structure has less symmetry. Bragg peaks at $\mathbf{Q}$ positions exist if the fluctuations of $\mathbf{x}^{\perp}$, for each node of the network, around the average orientation $\mathbf{E}$, expressed as $\langle \mathbf{x}^{\perp 2}\rangle=\langle|\mathbf{x}^{\perp}(\mathbf{x}^{\parallel})-(\mathbf{E}\mathbf{x}^{\parallel}+\bar{\mathbf{h}})|^2\rangle$, remain bounded as the system size tends to infinity.[18]

An application of previous ideas was carried out in two structures with C_{60} as the seed. The first structure was grown by choosing randomly between the 30 possible twofold sites, and 1691 centers of fullerenes were generated. For the second, the 20 possible threefold sites were selected randomly by obtaining 1216 centers of fullerenes. Both sets were separately lifted up to the six-dimensional space and the equations of the hypersurface was fitted by a least-squares method. In both cases, the values for $\mathbf{E}$ showed a slight deviation from the perfect icosahedral symmetry which should be reflected in the diffraction pattern by shifts of the peaks from icosahedral positions, as will be detailed in a forthcoming publication. In terms of the second-order invariants under rotation $|W_l|$,[19,20] the aperiodic structures considered (from 322 atoms up to 3792 atoms) presented high signals in $l=6$ which correspond to icosahedral symmetry. For icosahedral symmetry, $|W_6|=0.169\,75$, and for our structures the values varied from $|W_6|=0.143\,73$ to $|W_6|=0.166\,18$ which are considerably bigger than the value $|W_6|=0.013\,16$ for cubic systems. Also, important signals which correspond to cubic symmetry in $l=4$ were observed.

Figure 3 shows phason fluctuations as a function of the system size for the twofold and threefold cases. As can be seen, the fluctuations are unbounded, indicating that the diffraction pattern of the structure presents peaks with finite size. In view of the fact that no interpenetration is allowed, and given the random nature of the growth process, there are many cluster centers which are not connected to their neighbors by a bond with the proper length and orientation, i.e., the two-dimensional manifold in hyperspace is torn. This means that the

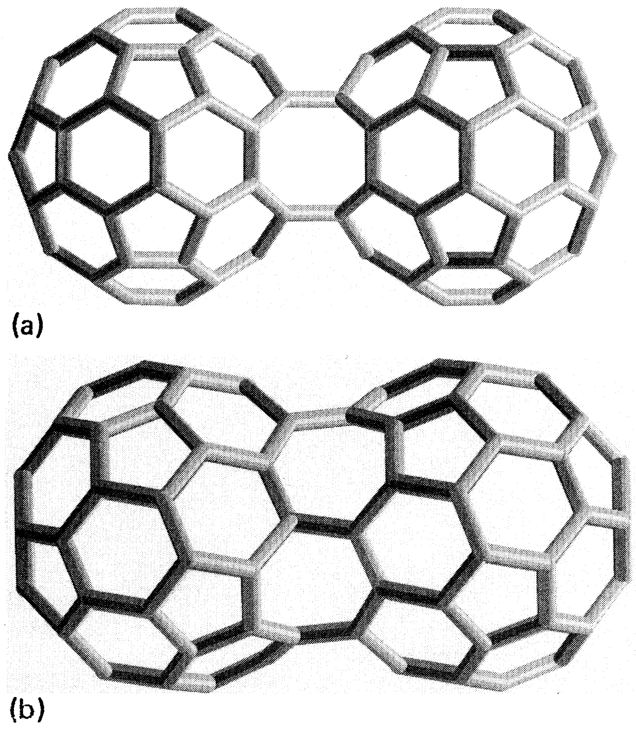

FIG. 2. (a) Two molecules of C_{60} joined by the twofold axis. (b) Two molecules of C_{60} joined by the threefold axis.

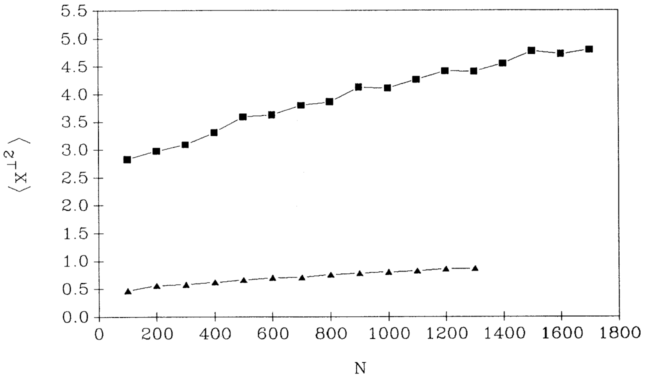

FIG. 3. Phason fluctuations versus system's size of the network of aperiodic graphite foams. Triangles and squares represent the threefold and twofold linkages, respectively. The unity of $\langle x^{\perp 2} \rangle$ are arbitrary.

structure is a strict icosahedral glass.[21]

The structures generated with this method are closed; however, open arrangements such as the periodic P graphite surfaces can also be obtained. Considering that the graphitic sheet is closed, it then has the same topology as the sphere, but in this case there are not only pentagonal rings, there are heptagonal and octagonal rings of carbon and the expression $N_5 - N_7 - 2N_8 = 12$ must be satisfied, where N_5, N_7, and N_8 are the number of pentagons, heptagons, and octagons, respectively. When two molecules of C_{60} are joined by the twofold axis, a structure with 116 atoms with 4 octagons, 20 pentagons, and 36 hexagons is obtained [see Fig. 2(a)]. If the molecules are joined by the threefold axis, a structure with 108 atoms, 6 heptagons, 18 pentagons, and 32 hexagons is built [see Fig. 2(b)]. The stability for these two cases and for the bigger aperiodic structures has been calculated using the potential proposed by Tersoff[22] with a relaxation program. When the two molecules share the twofold axis, the energy per atom relative to graphite ΔE is -0.5977 eV, and if the two molecules share the threefold axis, $\Delta E = -0.5594$ eV; for C_{60}, $\Delta E = -0.6887$ eV. All the aperiodic structures presented energies between $\Delta E = -0.53$ and -0.65 eV, so they are closer in energy to graphite than C_{60}.

Since the potential prefers graphitic bonds (bonds with 120° and 1.42 Å), it is clear that pentagonal rings with 108° cost more energy, so it can be argued that the fullerene C_{116} with 12 pentagonal rings is more stable than the structure with 116 atoms, 20 pentagons, and 4 octagons as mentioned above. This is true if there is no restriction on the size of the particle. In fact, the increase of the cohesive energy with the size toward graphite favors the driving force for the coalescence of fullerenes. However, when the fullerenes are in a lattice or in an aperiodic array, due to packing conditions there is a restricted space and the fullerene cannot have a bigger size. In this case, the structure with 8 octagonal rings and 20 pentagons will be preferred.

In summary, we have found aperiodic graphitic structures which are more stable than C_{60}. These structures are not crystalline nor amorphous. We think that due to the violent processes for generating fullerenes, structures not perfectly ordered as the ones described here are quite feasible. In addition, the method can be implemented to generate continuous random surfaces which can find application in the structure of microemulsions.

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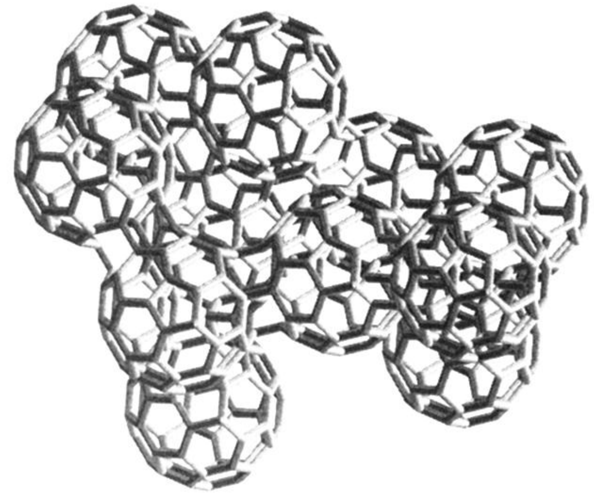

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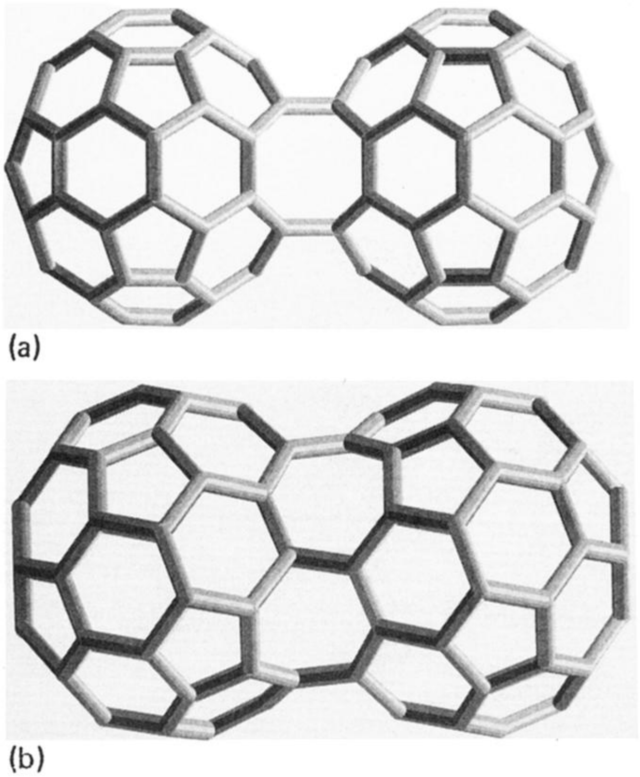

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